Advanced Technologies for Chemical Weapons Detection and Analysis

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2004 Scientific Conference on Chemical and Biological Defense Research, Nov. 15-17, Hunt Valley, MD

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy NNSA under Contract DE-AC04-94AL85000.

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Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **17 NOV 2004**	2. REPORT TYPE **N/A**	3. DATES COVERED **-**

4. TITLE AND SUBTITLE **Advanced Technologies for Chemical Weapons Detection and Analysis**	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Sandia National Laboratories Albuquerque, NM 87185**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR’S ACRONYM(S)
	11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM001849, 2004 Scientific Conference on Chemical and Biological Defense Research. Held in Hunt Valley, Maryland on 15-17 November 2004 . , The original document contains color images.

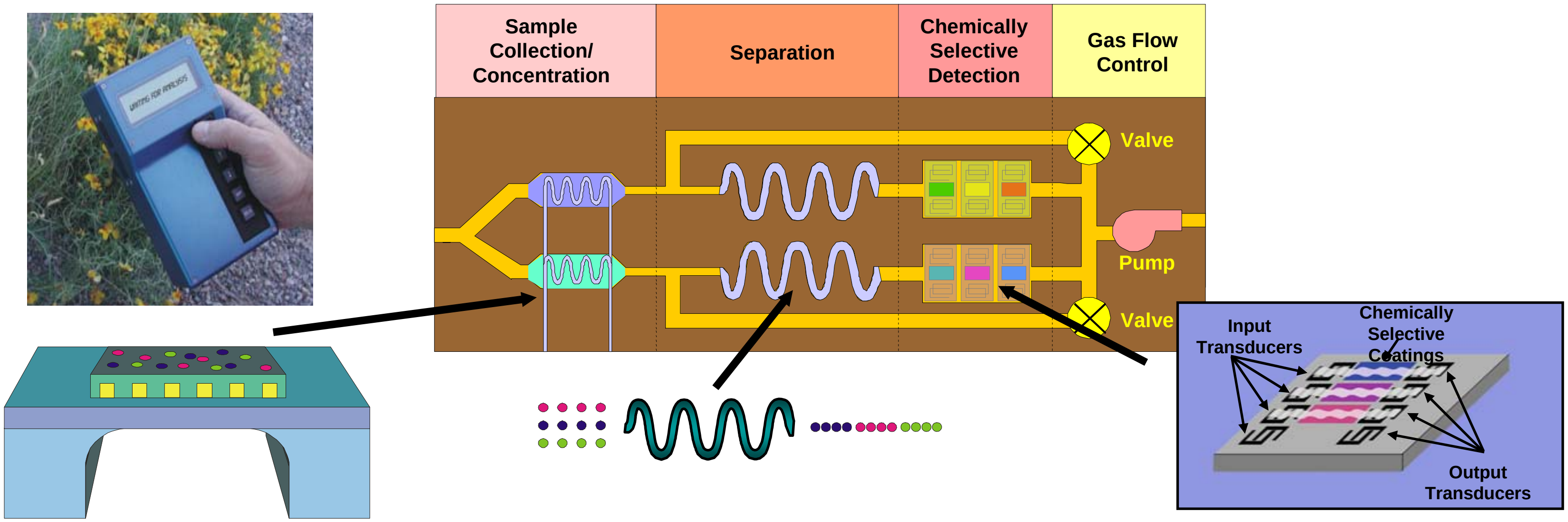
14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**UU**	**26**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

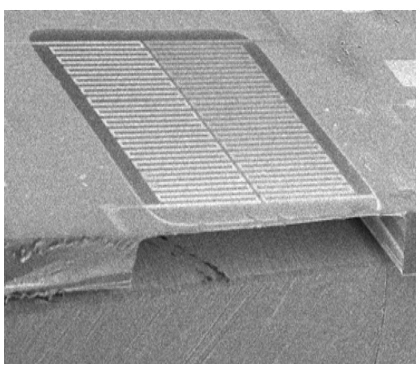
μChemLab™

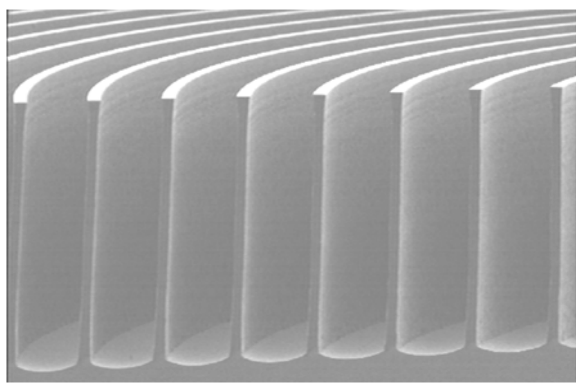


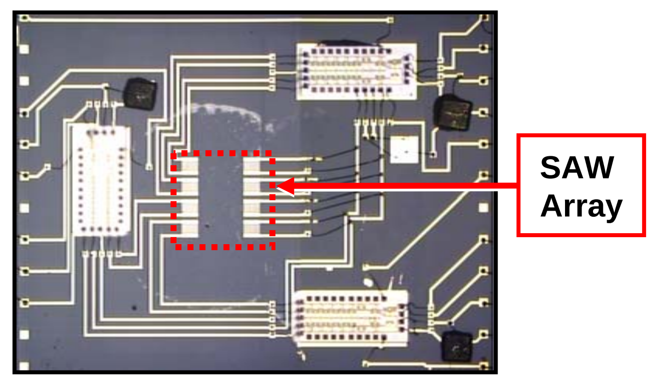
Preconcentrator accumulates species of interest

Gas Chromatograph separates species in time

Acoustic Sensors provide sensitive detection

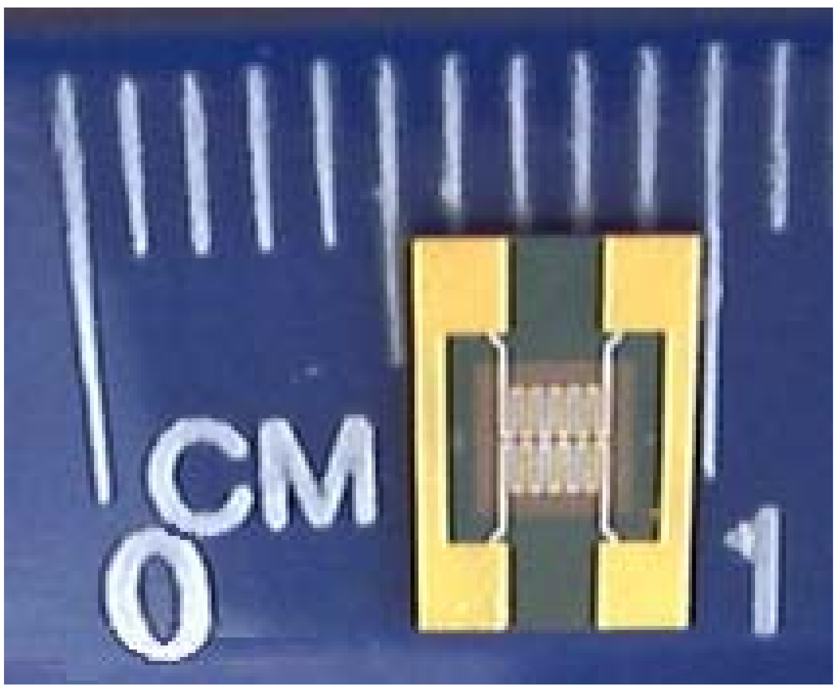


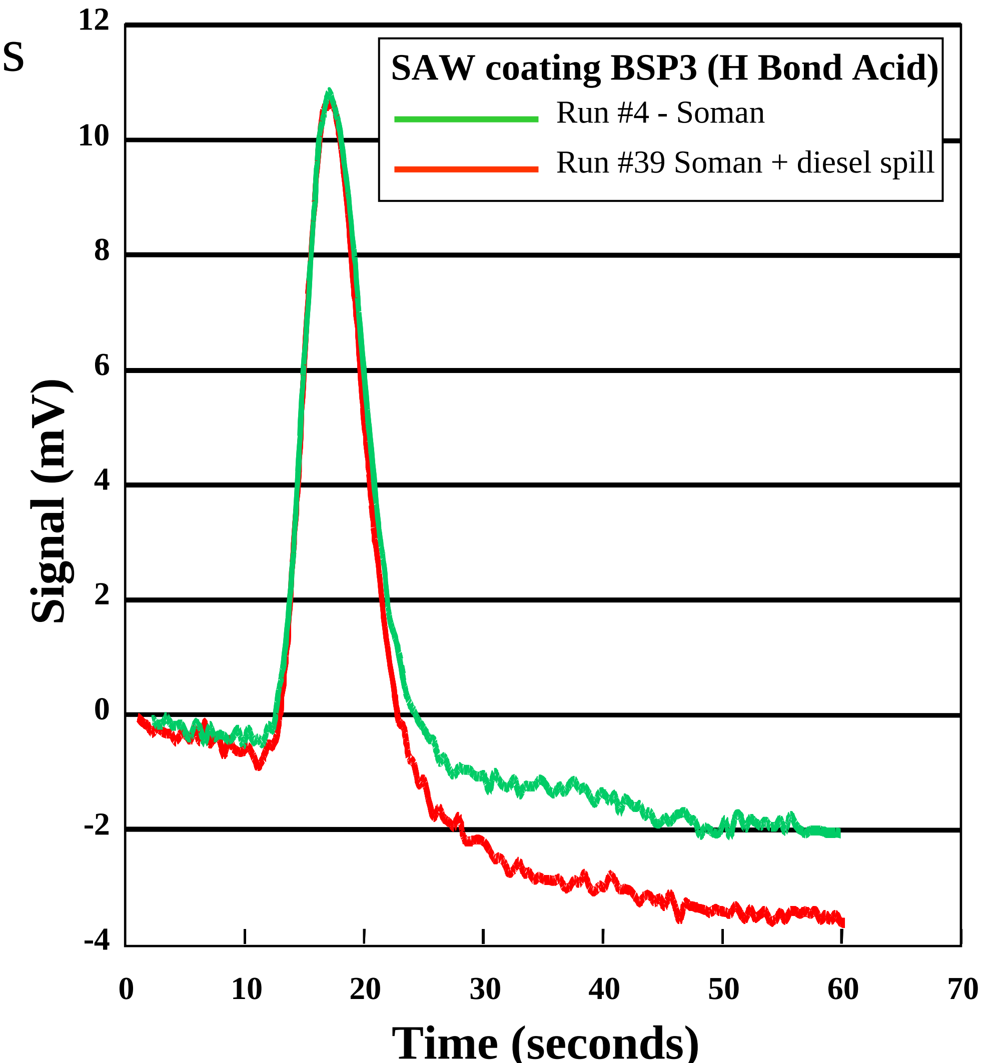




Preconcentrator Selectivity

- Adsorbent preconcentrates analytes
- Micro-hotplate rapidly heats to desorb trapped analytes
- Phosphonates selective sol-gel material for CW agents





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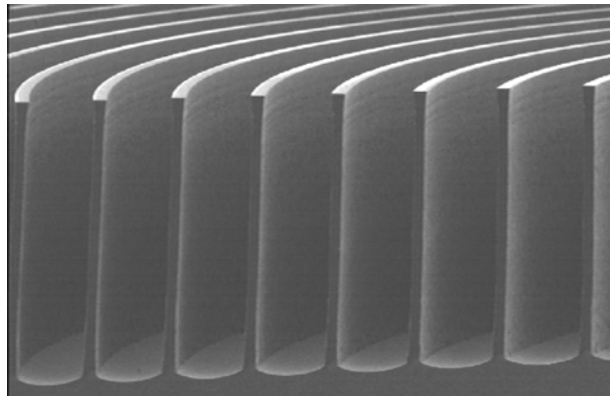
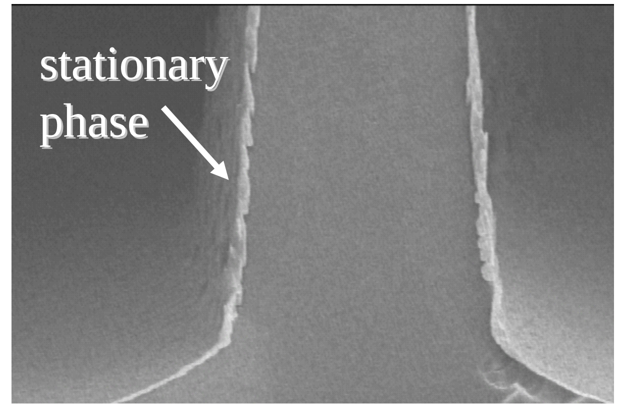
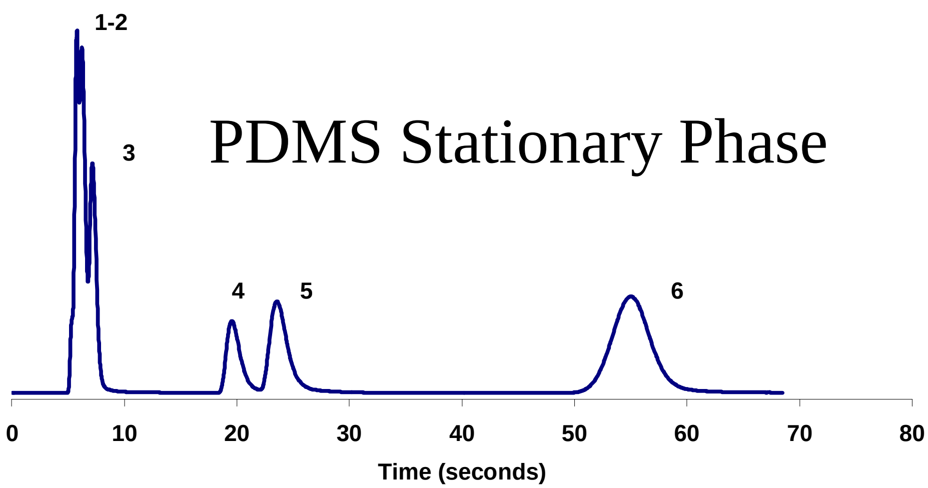
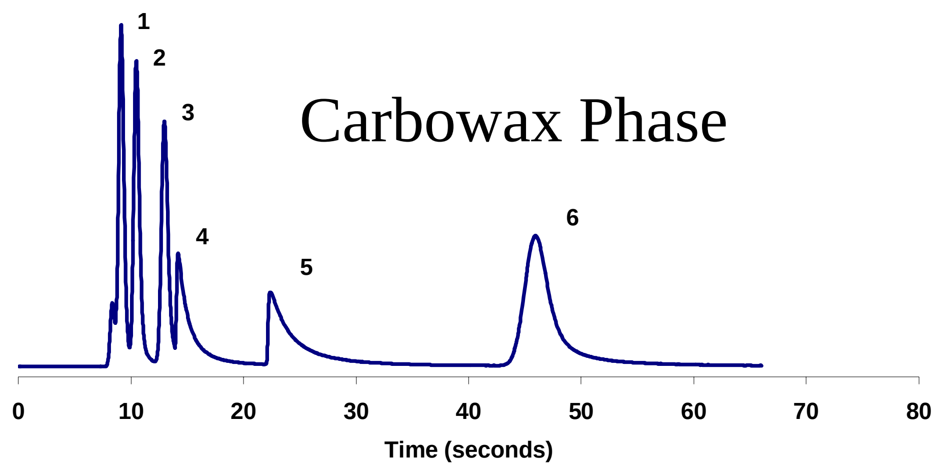
Micro-GC Performance

SEM of Deep Etch Spiral GC Column









1) benzene 2) toluene 3) xylene
4) DMMP 5) DEMP 6) methyl salicylate

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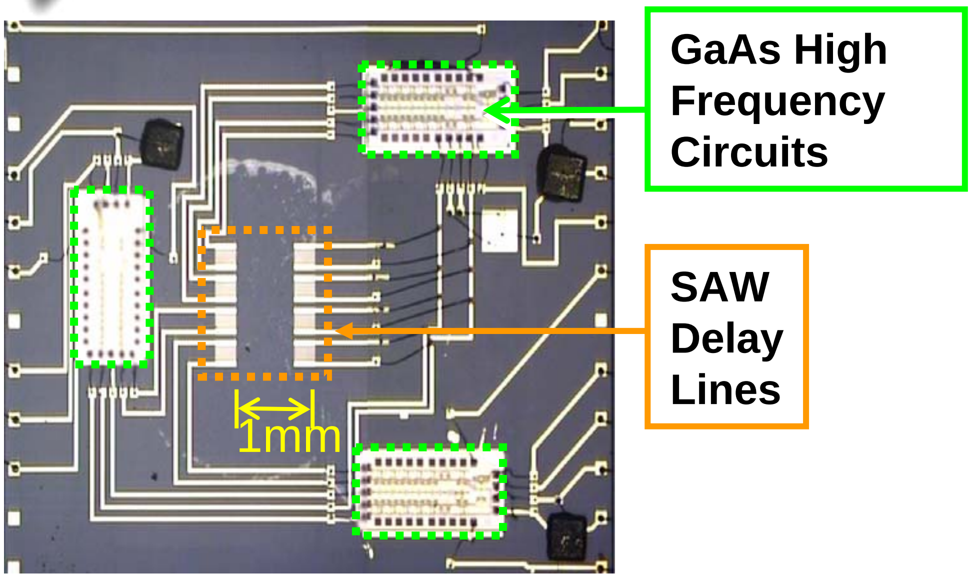
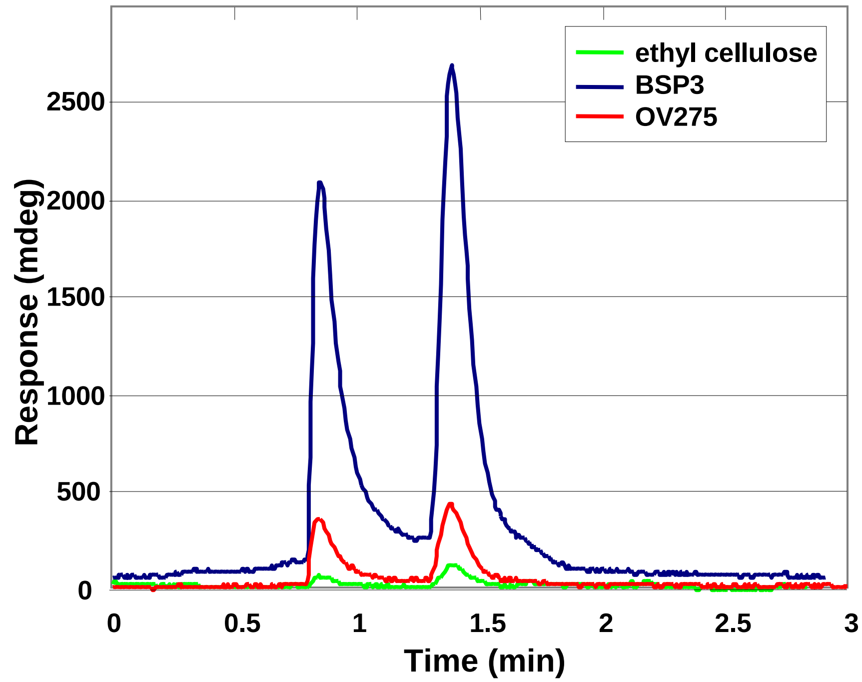
SAW Description





<u>SAW Sensor Array</u>

- Drive electronics lock in on REFERENCE resonance to drive delay lines in array
- Receiver electronics compare phase of drive and received wave frequencies
- Coatings on the delay lines selectively absorb analytes in gas stream over array
- Mass change on the quartz surface affects the phase difference
- Input power 3 VDC at 100 mA
- Output differential –0.9 VDC to +0.9VDC proportional to phase

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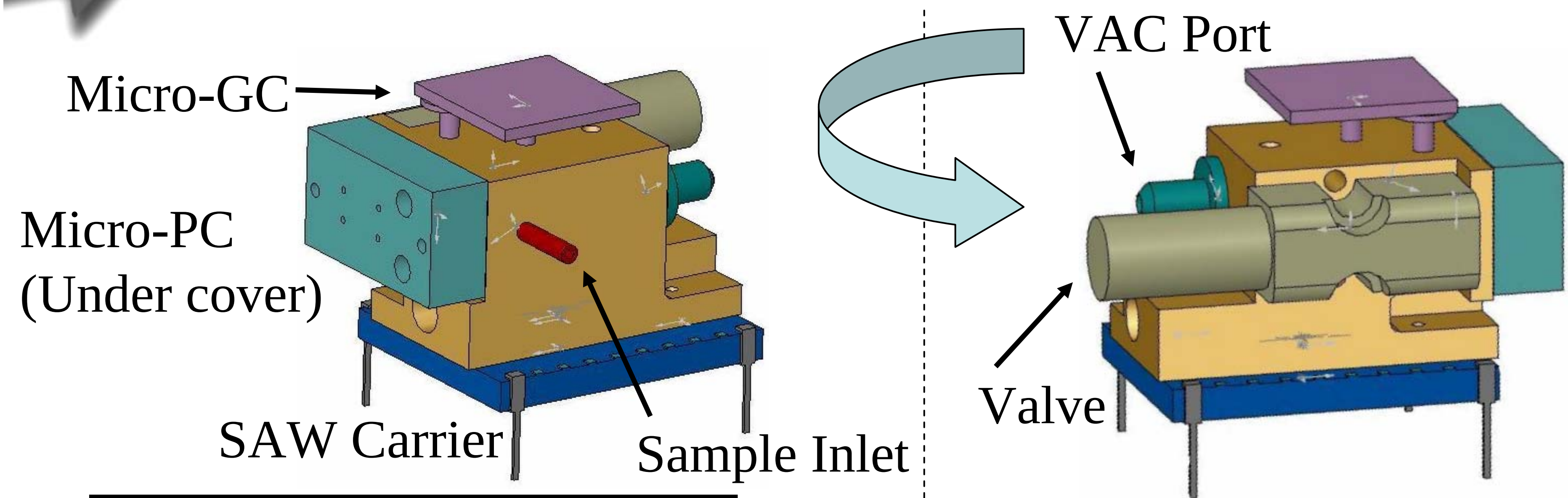
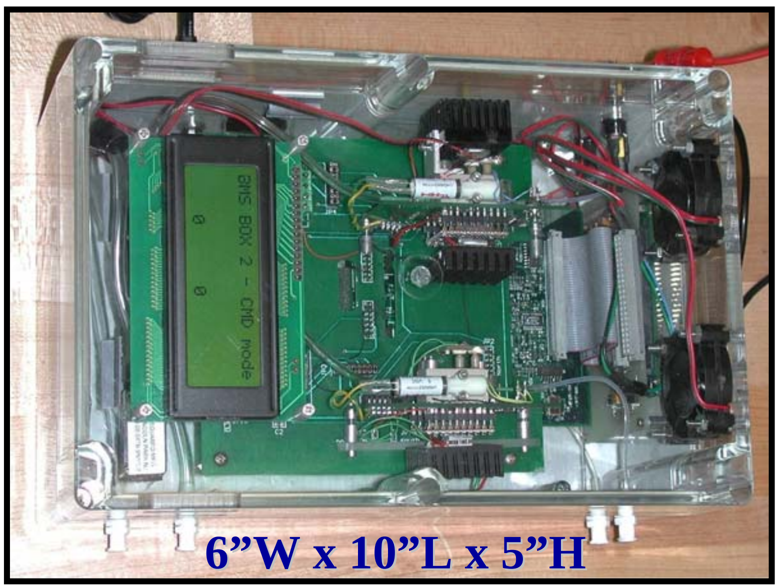
µChemLab Bug

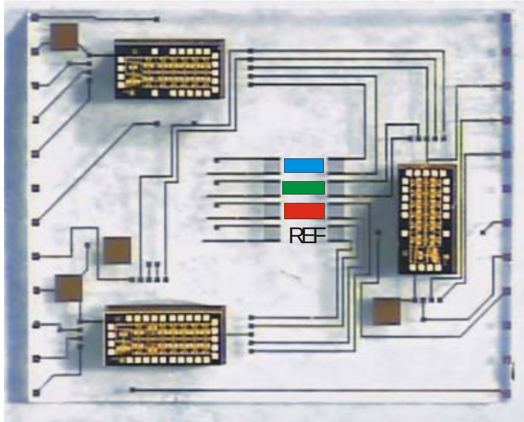




SAW Shortcomings

SAWs Are Great micro-Balances; Only a Few Drawbacks

- Hybrid architecture – Quartz substrate, GaAs electronics
    - -Monolithic integration with PC and GC is difficult
    - -High labor cost
- 100-500 MHz operating frequency
    - -COTS electronics more complicated to use
    - -Power hungry (~300 mW for detector)
- Polymer coating is difficult
    - -Small application area (0.3 mm x 0.8 mm)
    - -Coating must have intimate contact with quartz (little beading, no dewetting)
    - -Sensitive to overload
- Finite time for sample absorb/desorb
    - - Wider peaks hamper chromatography



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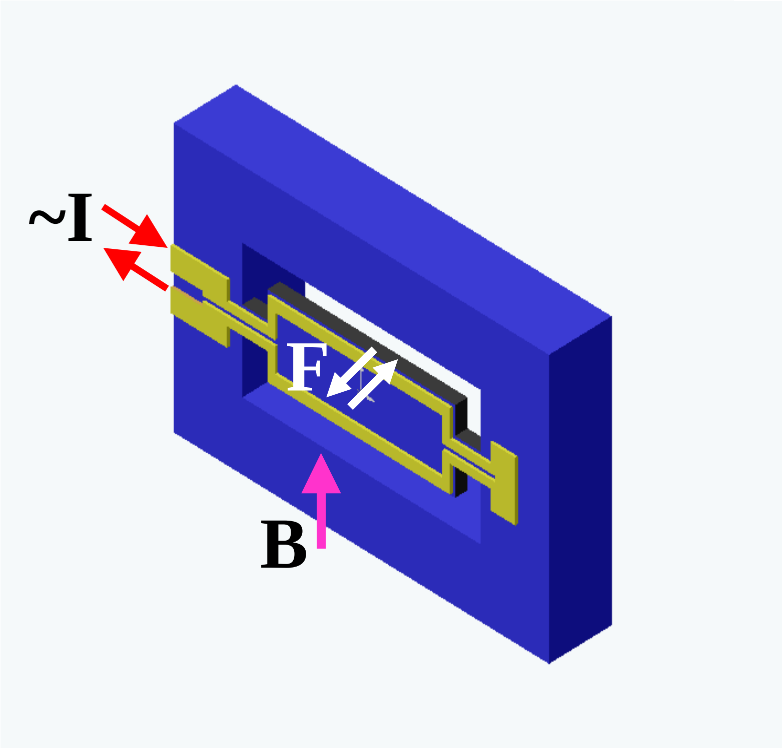
New Micro-Sensors

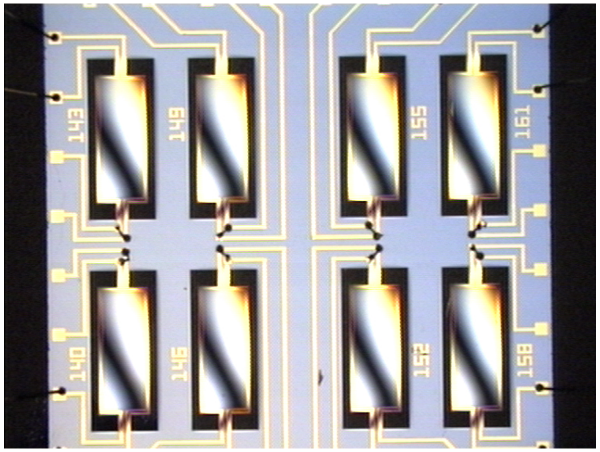
- Pivot Plate Resonator (PPR)
- Nano-Particle Ligand Bridge Sensor (NPLB)
- Nitrogen Phosphorus Detector (NPD)
- Thermal Conductivity Detector (TCD)
- Flame Ionization Detector (FID)
- Chemiresistors
- Pellistor Array
- Micro-Calibration Chip

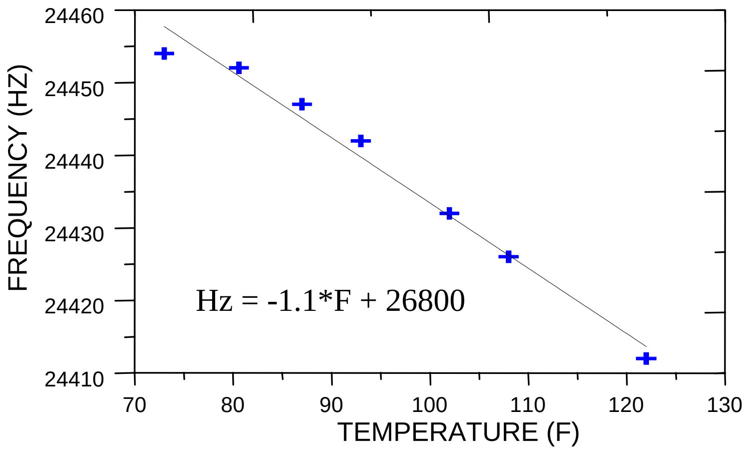
Pivot Plate Resonator (PPR)

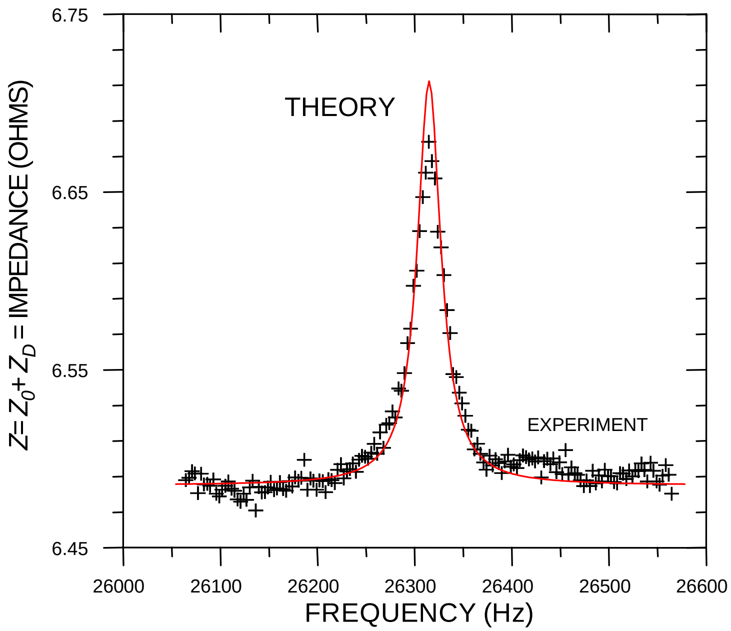


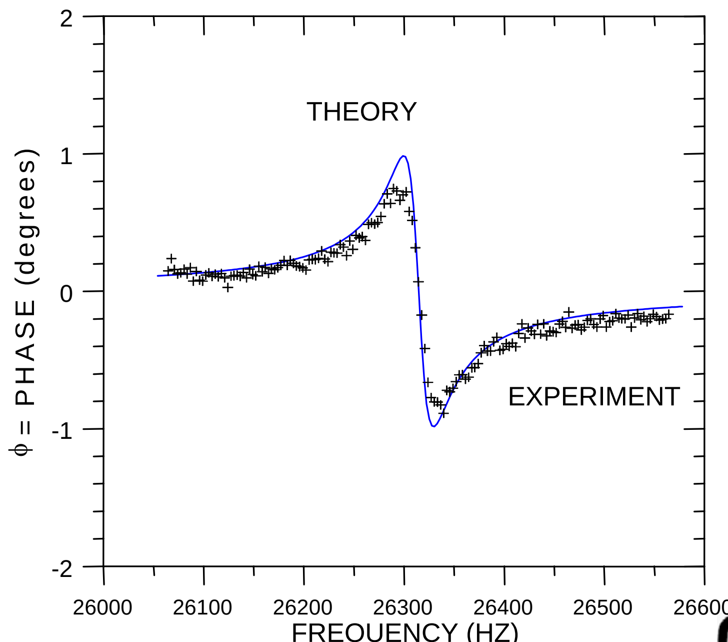
- Paddle supported on two pivots
- Pivots provide torsional spring force
- Current in magnetic field imposes a moment on the paddle
- Alternating current drives paddle into resonance
- Motion of paddle creates back-EMF
- Mass changes on paddle alter the resonant frequency
- Damping changes on paddle alter the amplitude of oscillation

PPR Testing









PPR – Pivot Plate Resonator

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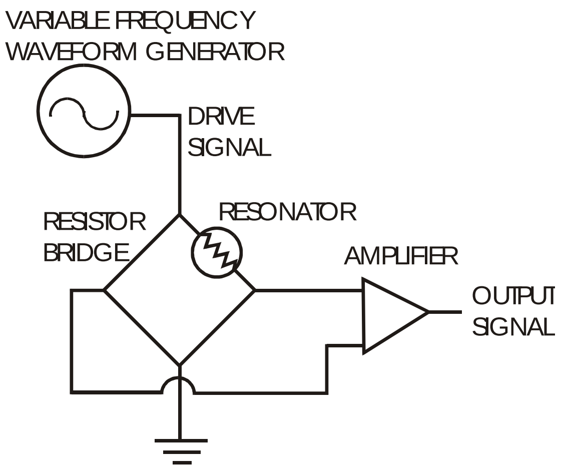
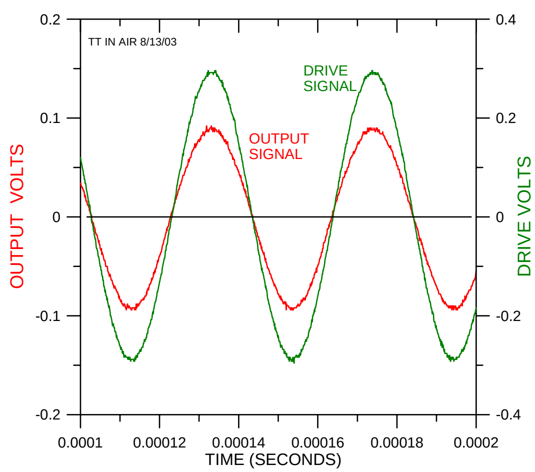
Mass Loading of a PPR

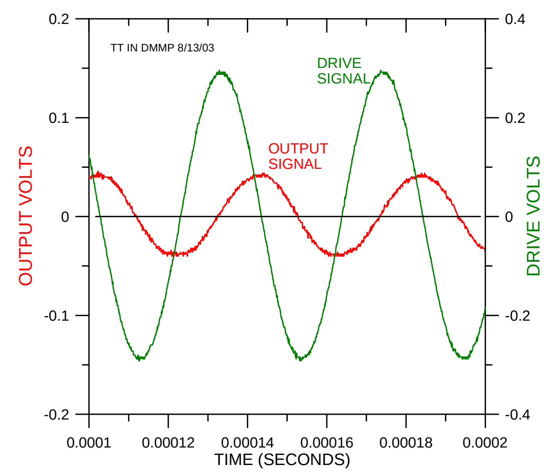


- Monitor phase for low level detection
- 10 ng causes about 90 degree phase shift
- Sensitivity about 9 degrees/ng
- Compare to minimum SAW sensitivity of about 0.1 ng

Coated paddle with no analyte



Response to Vapor Exposure



PPR – Pivot Plate Resonator

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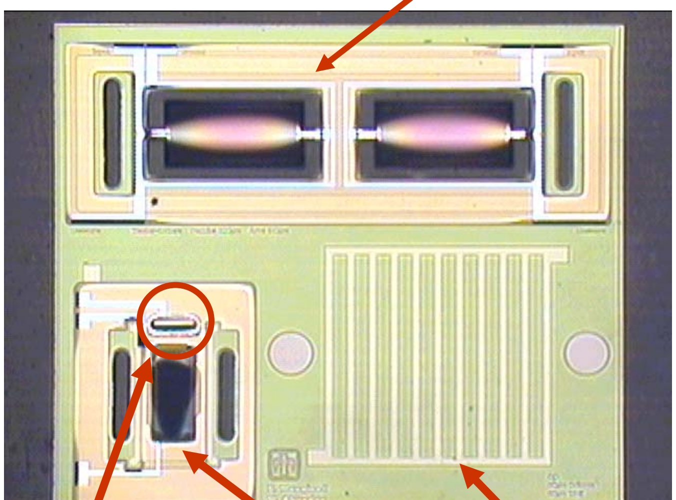
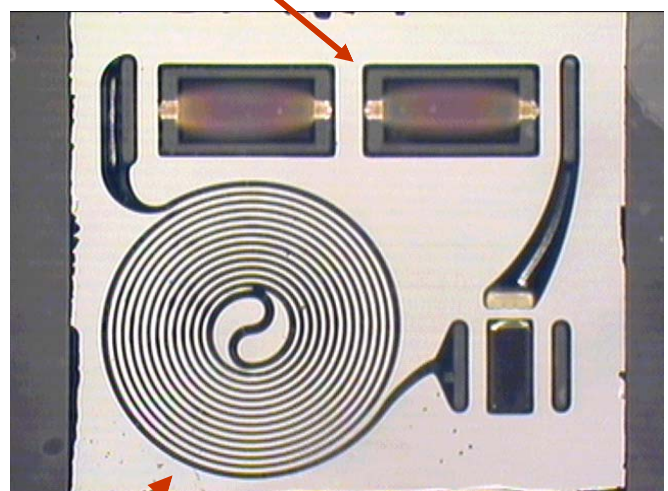
Integrated System with PPR

PC-GC-PPR System

Goal: monolithic integration

Pivot Plate Resonators





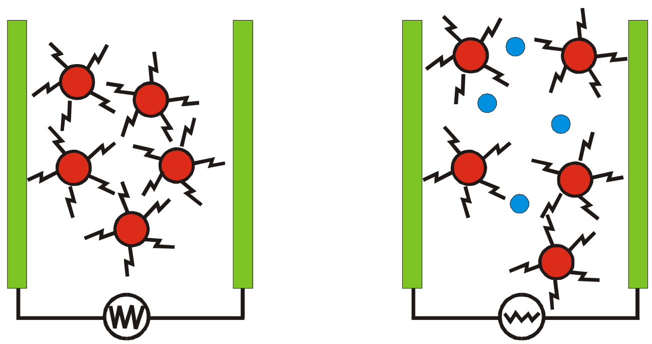
micro-Valve

PC

GC Column

PPR – Pivot Plate Resonator

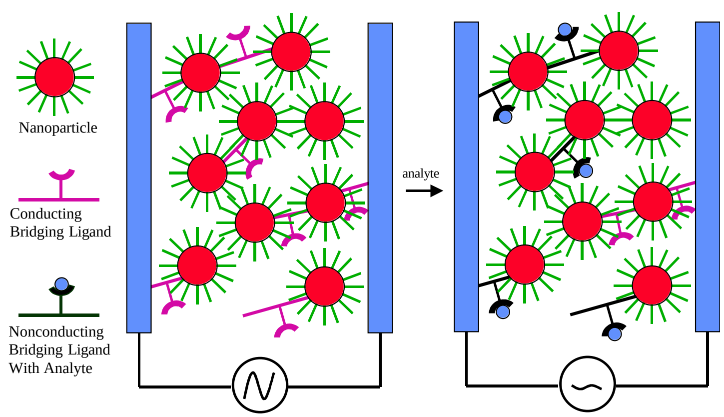
NanoParticle Ligand Bridge (NPLB) Detector



<u>NanoParticle Chemical Resistors</u>

Analyte absorbs in thin particle–loaded film. Film **<u>swells</u>** and separates particles reducing conductivity

Small Particle Array
Limited Number of Communication Paths



<u>NPLB Detector</u>

Analyte binding to pi-conjugated bridging ligand **<u>reduces current flow</u>** by perturbing the bridging ligand's conductivity.

NPLB – Nano-Particle Ligand Bridge sensor

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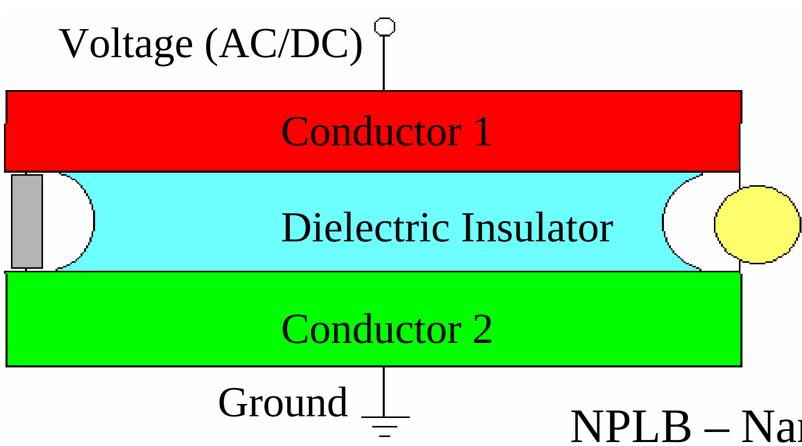
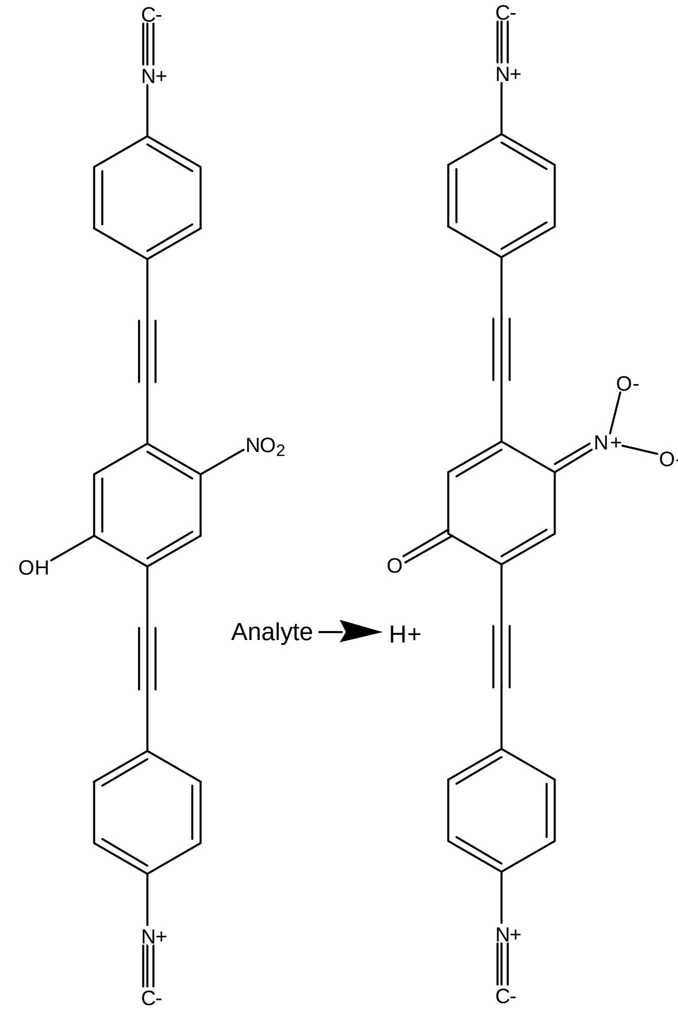
NPLB Construction

- Molecular wires control electronic communication between particles.
- Poly-nitro-phenol chains show high specificity for phosphonate groups
- Sulfur functionalizing end chains permits attachment to gold nanoparticles
- Difference in Homo/LumoGaps = 0.35 eV





More Conductive

Less Conductive
due to cross conjugation

NPLB – Nano-Particle Ligand Bridge sensor

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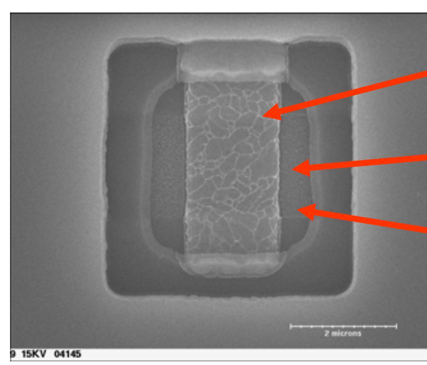
NPLB Construction

NPLB – Nano-Particle Ligand Bridge sensor

- Nanogap electrodes made through MEMS fabrication techniques
- Small ensemble of nanoparticles assembled between two nanoelectrodes -- particles migrate and structure under influence of an *AC* field.
- Ensemble stabilized by surfactant replacement -- weak bonds on nanoparticle replaced with tighter binding ligands (thiols or isocyanides)
- Limited percolation paths increases the sensitivity of the device. An ensemble with a large number of paths responds to a wider range of analyte concentrations before saturating.



poly-silicon

NPLB in gap

(+) semi-conductor

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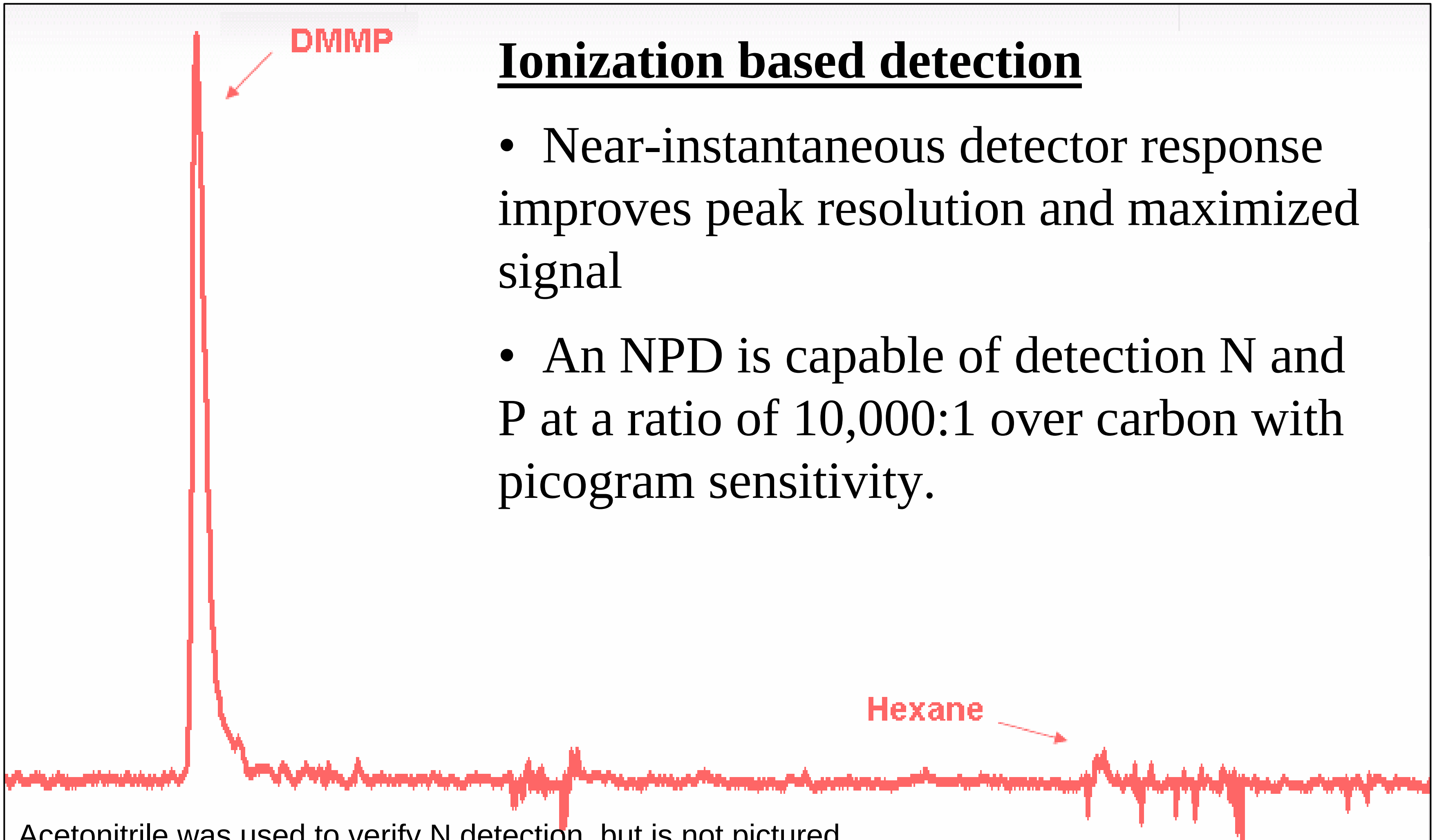
Nitrogen-Phosphorous Detector



Ionization based detection

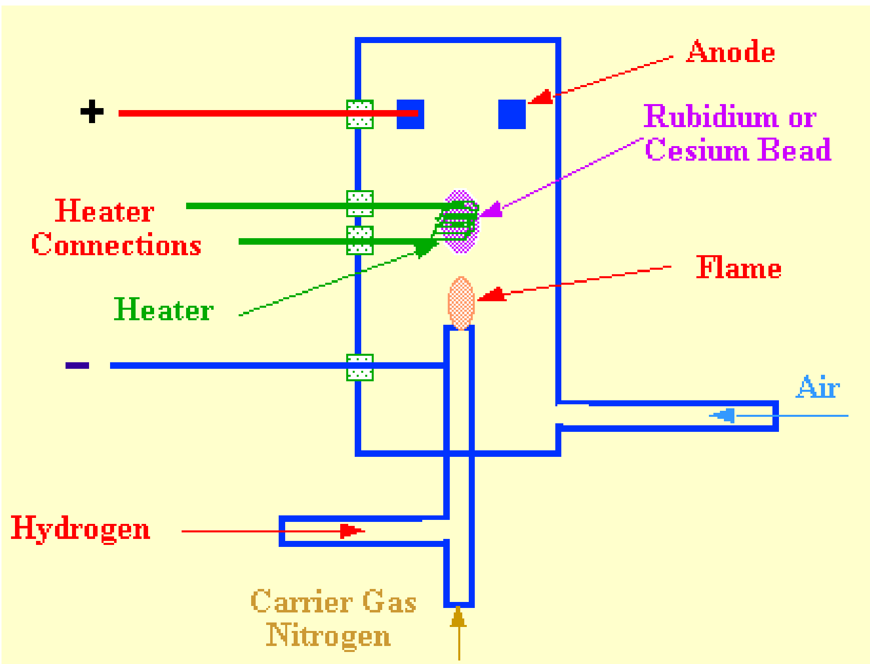
- Near-instantaneous detector response improves peak resolution and maximized signal
- An NPD is capable of detection N and P at a ratio of 10,000:1 over carbon with picogram sensitivity.

Acetonitrile was used to verify N detection, but is not pictured.

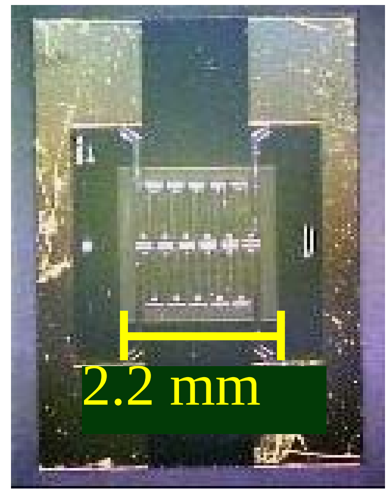
NPD – Nitrogen Phosphorus Detector

Sandia's Micro-NPD

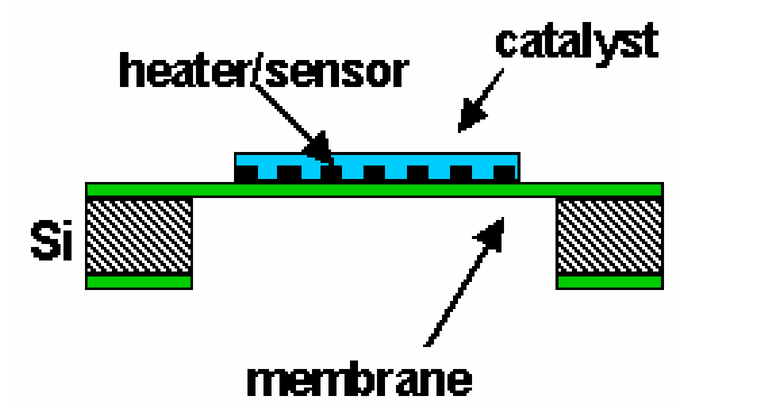
Commercial NPD



Uncoated



Coated



Sandia's micro-NPD has equivalent selectivity as commercial NPDs in a much smaller package. Electrodes will eventually exist on planar substrate.

NPD – Nitrogen Phosphorus Detector

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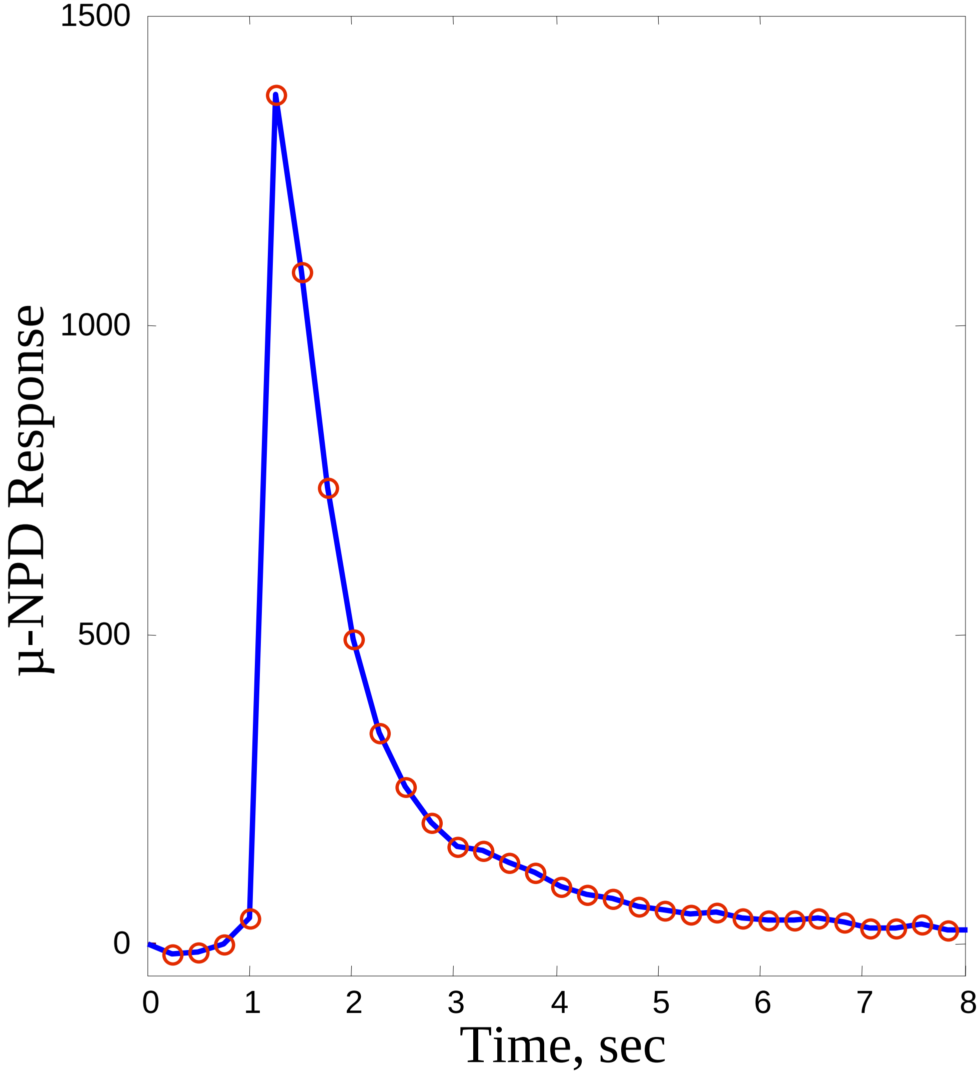
μChemLab with μNPD

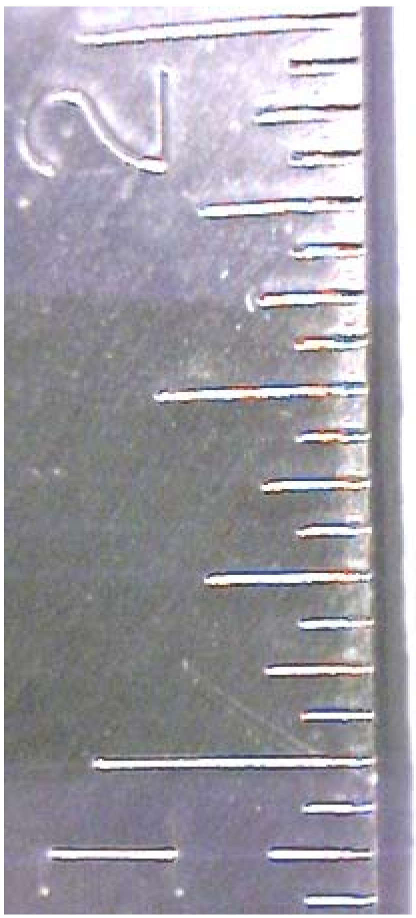


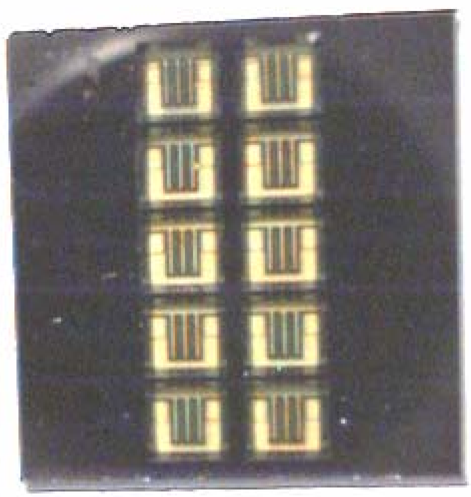
NPD – Nitrogen Phosphorus Detector

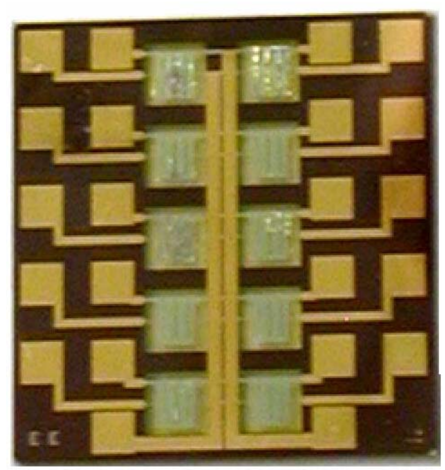
- μNPD and SAW sensors in μChemLab
- Low-level nitrated hydrocarbon analyte collected for 60 seconds
- PC decomposes analyte upon thermal desorption
- μNPD shows excellent response to resulting NOx products.
- 4 Hz DAQ rate too slow (may have missed peak)

Micro-Calibration Chip

- **10 Element Calibration Array** for retention time and sensor response
- Thin silicon nitride membrane (1 micron)
- Thermally labile chemical placed on each membrane
- Patterned metal heating element flash decomposes the chemical, injecting products into the GC column







Micro-Calibration Chip

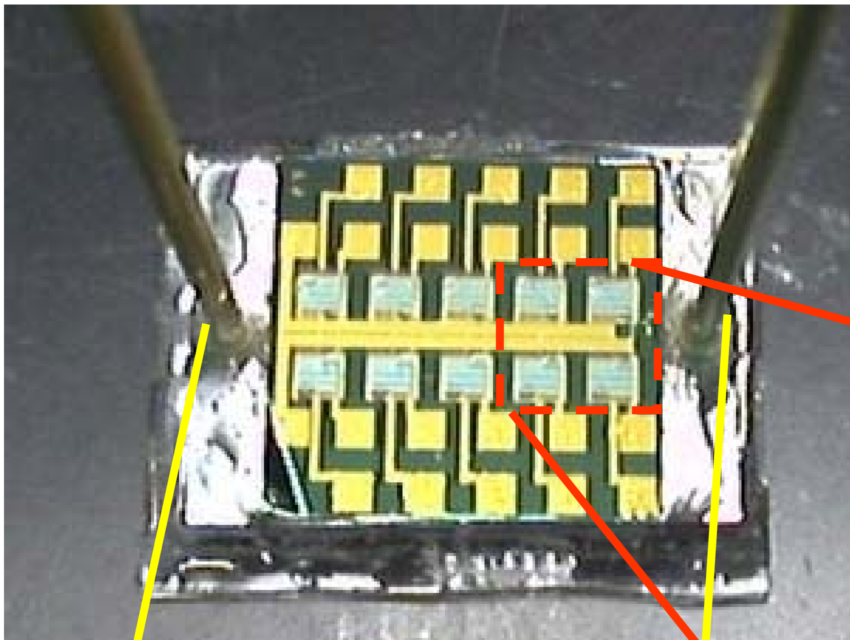
Construction/Coating

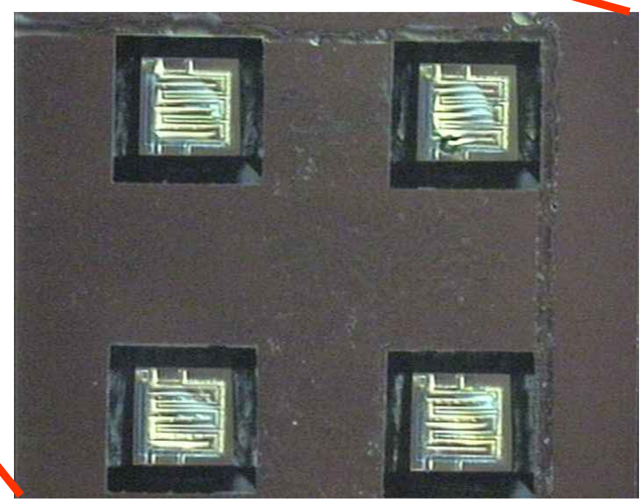
tetrapropyl ammonium hydroxide

$[N(C_3H_7)_4]^+ [OH]^-$

tripropyl amine + propene + water

$N(C_3H_7)_3 + C_3H_6 + H_2O$





Micro-Calibration Chip

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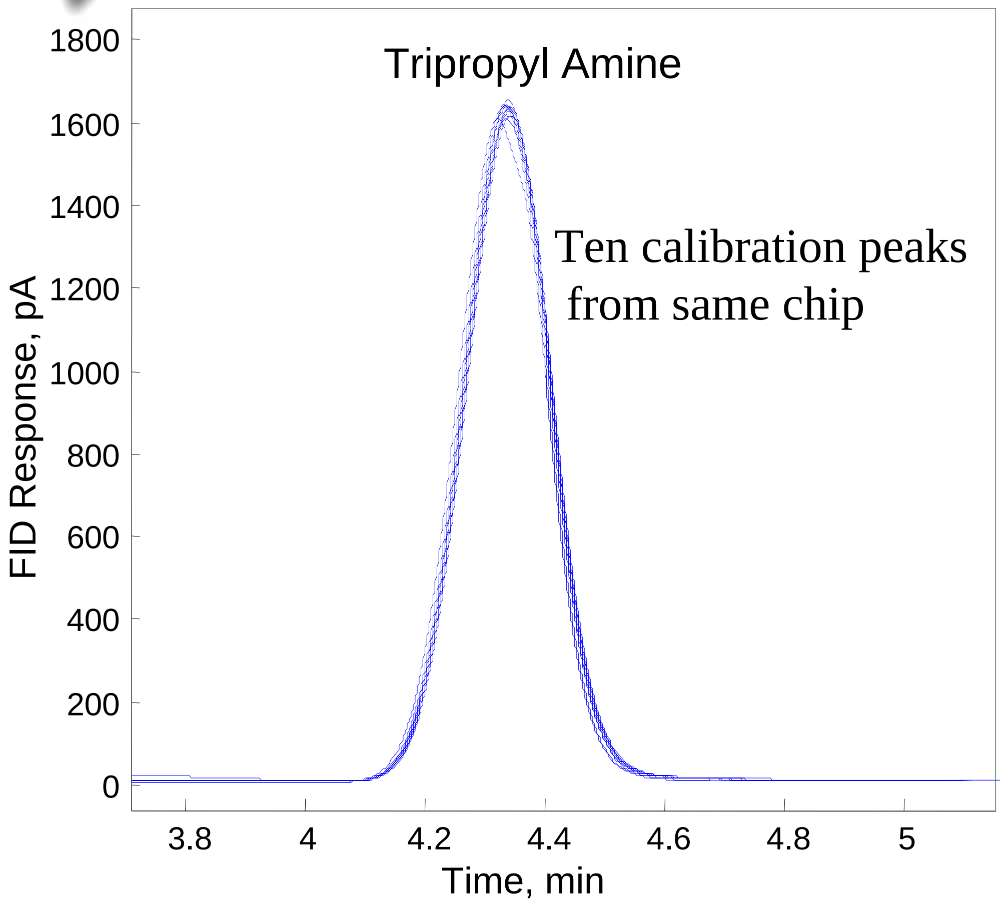
Micro-Calibration Chip



Fluidic fixturing pieces were HMDS treated prior to fixture assembly. Air carrier at 7 p.s.i., flow rate 11 ccm, oven 60C, 15-m DB-1 megabore column, FID.

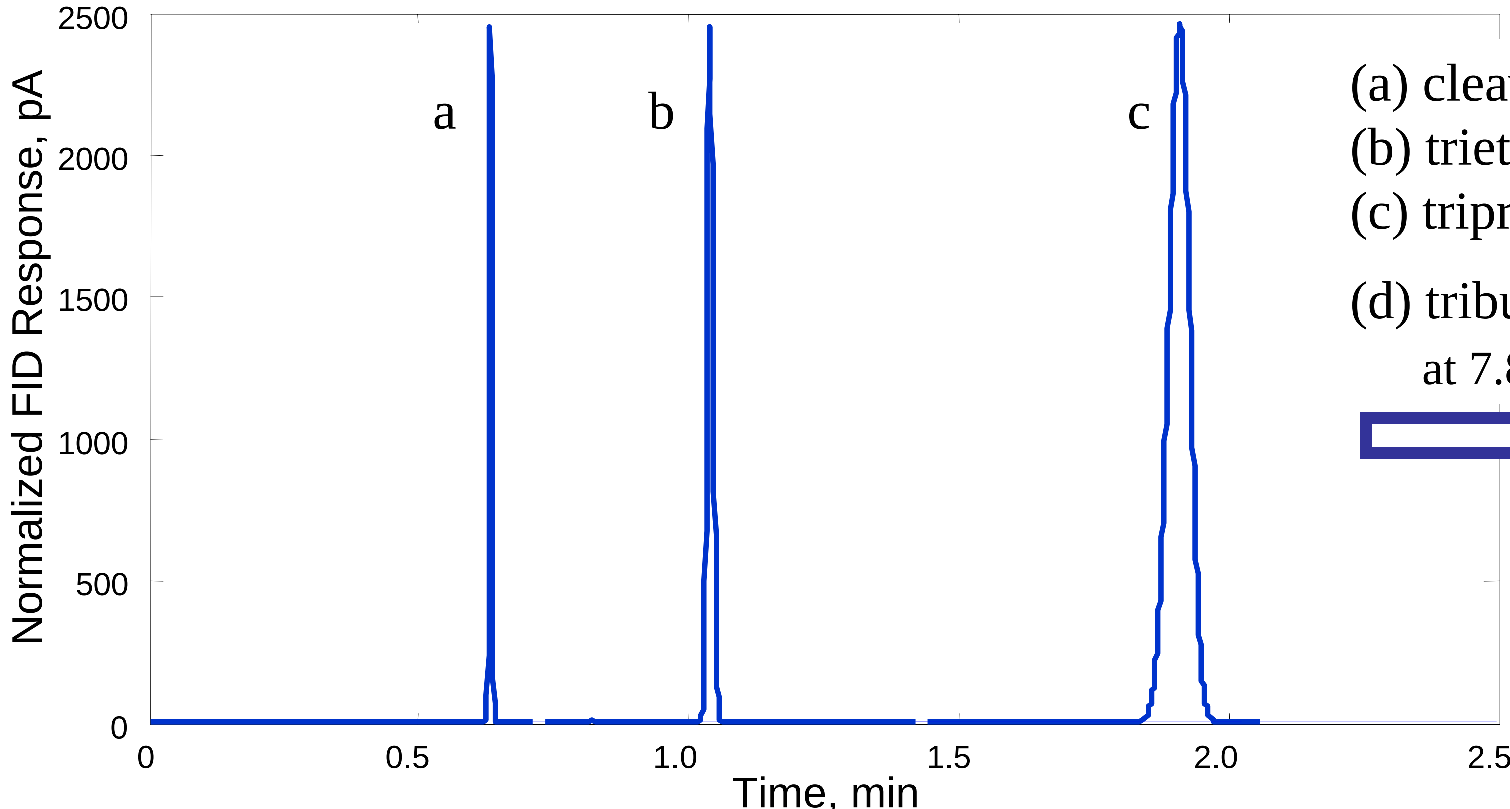
Reproducibility (one chip)

- Mass flux: 0.5%
- Peak height: 1.0%
- Peak Width: 1.3%
- Retention Time: 0.14%

Reproducibility (between chips)

- Mass flux: 5%
- Peak height: 5.5%
- Peak Width: 0.06%
- Retention Time: 0.8%

Calibration Markers



(a) cleaved alkene
(b) triethylamine
(c) tripropylamine
(d) tributylamine at 7.8 min

Air carrier at 5 p.s.i., flow rate 11 ccm, oven 100ºC, 15-m DB-1 megabore column, FID.

- Calibration marker(s) chosen to best match analytical task.

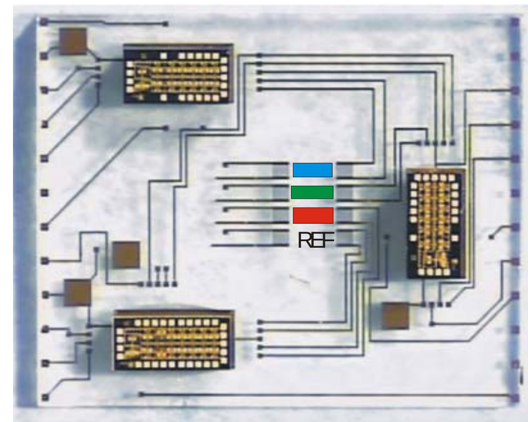
Summary and Conclusions

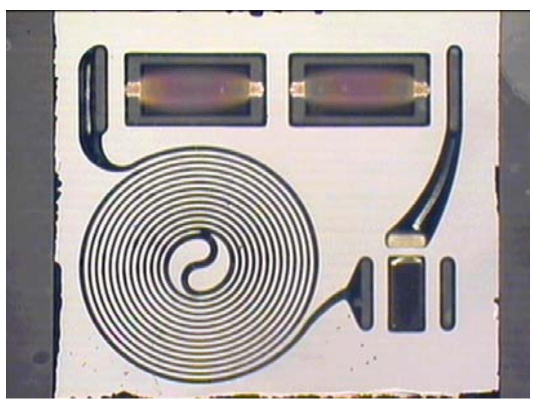
• Basic micro-ChemLab uses preconcentration, separation and detection stages

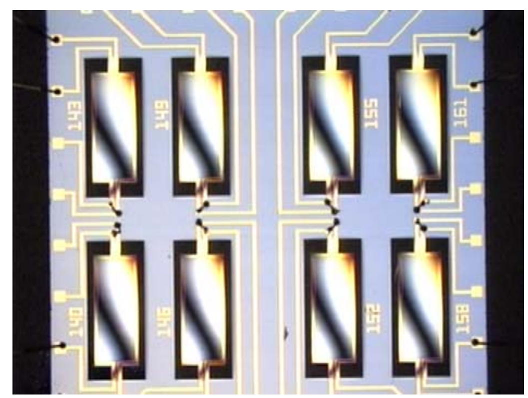
• Currently we use a hybrid integration of these stages

• Ultimate goal is to integrate these stages on a single substrate

• New sensor technologies will allow this full integration







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Summary and Conclusions

<u>Desired Features for Future Detectors</u>

- Monolithic integration – low cost, rapid production, no assembly
- Simple operation – simple electronics, little/no post-fabrication steps
- Low power – long life in field portable applications
- Rapid response – higher chromatographic resolution
- Low noise and high sensitivity (picograms)
- Arrayed response – better analyte discrimination, low false-alert

<u>Sensors Under Investigation – Operating Mechanism</u>

- Pivot Plate Resonator (PPR) – microbalance
- Nano-Particle Ligand Bridge (NPLB) – electrical conductivity
- Nitrogen Phosphorous Detector (NPD) – thermionic ionization

<u>Also</u>: Microcalibration device for GC and sensor calibration

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Behind the Scenes

Acknowledgements

Steven Showalter – NPD coatings

Jim Barnett – NPD device testing

James Sanchez – general microfabrication

Joseph Bauer – PPR integration and microfabrication

Jennifer Ellison – microcalibration device testing

John Dickenson – PPR testing and software

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PPR Theory

$$J\,\ddot{\boldsymbol{\theta}} + C_t\,\dot{\boldsymbol{\theta}} + k\,\boldsymbol{\theta} = \mathbf{T},$$

$$\mathbf{T} = T\exp(j\omega\,t) = B\,wL\,I\exp(j\omega\,t) = B\,wL\,\mathbf{I},$$

$$J = \rho\,w\,c\,L\left(c^2 + L^2\right)/12$$

$$k = 2\,\beta\,b\,c^3 G/a, \quad \beta = f(b/c) \approx 1/3$$

$$C_t = damping\ coef. = \sqrt{k\,J}\big/Q = 2\,\varsigma\,\sqrt{k\,J}$$

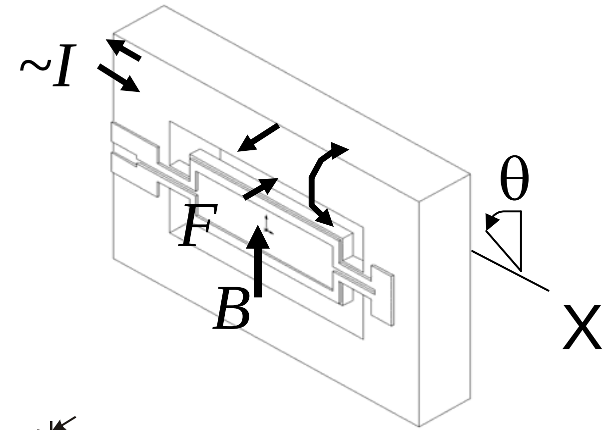
solution:

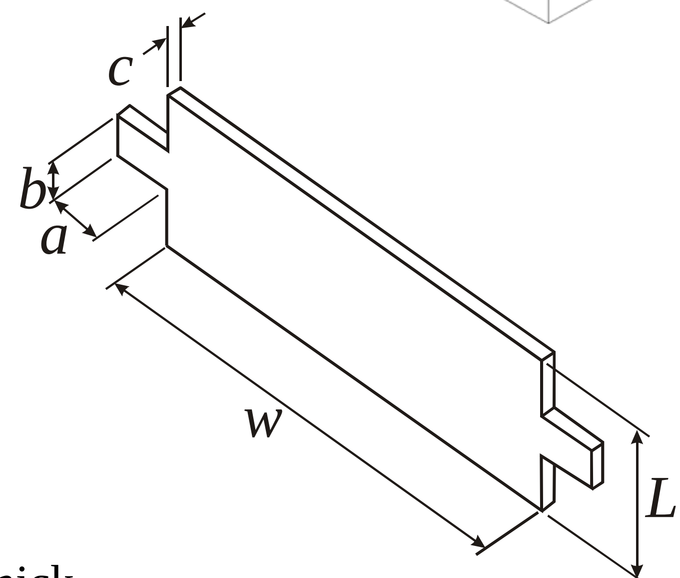
$$\omega_n = \sqrt{k/J} = \sqrt{\frac{8\,b\,c^2 G}{\rho\,w\,a\,L\left(c^2 + L^2\right)}},$$

$$r = \frac{\omega}{\omega_n},$$

$$\mathbf{Z} = \frac{\mathbf{V}}{\mathbf{I}} = R_0 - \frac{B\,wL\;j\omega\,\overline{\Theta}}{I} = R_0 + \frac{j\omega\,(B\,wL)^2/k}{1 - r^2 + 2\,r\,\varsigma\,j}$$

$$= |\mathbf{Z}|\exp(+\,j\phi_Z)$$





Typical Paddle: 1500μm wide x 600μm tall x 10μm thick

Typical Tab: a = 200μm; b = 160μm; c = 10μm   Resonant Frequency = 26kHz

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